AB-INITIO COMPUTATIONS OF HOLE TRANSPORT AND EXCITONIC PROCESSES IN INORGANIC SCINTILLATORS

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ABSTRACT

To guide the continuing experimental search for improved scintillators for gamma-ray detection in medical imaging., we have used *ab-initio* quantum chemistry codes and high-performance computers to model processes critical for scintillation in inorganic crystals. These processes include the formation of lattice-relaxed holes, the diffusion of holes through the host crystal, and the formation of excited electronic states. Materials investigated thus far include CsI, Tl- and Na-activated CsI, and two lead compounds, PbF_2, and PbF_4.

INTRODUCTION

This work is motivated by the need for improved scintillators for gamma-ray detection in medical imaging. To guide the continuing experimental search, we are investigating the use of *ab-initio* quantum chemistry codes and high-performance computers to model processes critical for scintillation in inorganic crystals. These include both activated scintillators, such as NaI:Tl, CsI:Na, CaF_2:Eu, and Lu_2SiO_5:Ce where the ionizing energy diffuses through the host crystal and produces an excited state at or near an activator atom, and self-activated scintillators, such as CsI, NaI, $Bi_4Ge_3O_{12}$, CeF_3, BaF_2, and $PbWO_4$, where the activator atoms are a major constituent of the crystal and/or excitonic processes are involved.

The scintillation process (radioluminescence) (1) is more complicated than that of photoluminescence. When high energy ionizing radiation is absorbed by a material, a large number of electrons and holes are created. The diffusion of ionization energy (electrons and holes) through a host crystal leads to the formation of excitons and trapping centers and, in the case of activated materials, to the capture of these charge carriers in the vicinity of an activator atom. For activated scintillators hole trapping and transport are of critical importance for efficient scintillation.

To treat hole trapping and transport, the crystal is modeled by a central cluster of atoms embedded in a lattice of point charges chosen to provide the same electrostatic ionic field as in the infinite crystal. The recent advent of high-performance computers has made it possible to perform *ab-initio* electronic structure calculations on reasonably large clusters (≈50 atoms) which are sufficiently large to allow a proper representation of the relaxed states of the system. Only unit cell information is required to select the cluster atoms and to determine the coordinates of the cluster atoms and the surrounding point charges.

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Choice of Atom Cluster and Surroundings

The first crucial choice to be made for the successful modeling of hole relaxation, hole transport, and exciton formation in crystalline materials is the size and composition of the atom cluster. The choice of cluster has to be carefully balanced between cluster size and computational cost. A cluster that is too small would not allow for proper relaxation. Our general strategy is to surround the active cluster region (which will include an activator) with movable quantum atoms, which in turn are surrounded by fixed quantum atoms.

To reproduce the electrostatic potential in the infinite crystal, the cluster is embedded in a large point charge array. We have developed a method for finding arrays of point charges located at normal lattice sites that reproduce the electrostatic Madelung potential at more than 100 randomly chosen point in cluster volume with a rms error of less than 1.0 mV (2). The method consists of the following steps: (i) Construct a $2N \times 2N \times 2N$ lattice of unit cells, assigning cluster atoms to the central volume and point charges to the rest; (ii) Compute the Madelung potential (using the Ewald method) at each cluster atom and at 100 randomly chosen points in the cluster volume; (iii) Set up a system of linear equations that relates the values of the several thousand outer point charges to the electrostatic potential produced by all the charges at the reference points in step (ii); (iv) Solve for the values of the outermost point charges that most closely reproduce the Madelung potential in the cluster volume. The resulting, highly under-determined, linear system of equations is solved for in a minimum norm least squares sense using a complete orthogonal factorization of the matrix. A standard singular value decomposition (SVD) of the matrix could, of course, also have been used. A typical charge array consists of a total of 10,000 point charges with 3,000 outermost charges varied by $|\Delta q| < 0.3$ units from their standard values. Note that there are several thousand ions between the atom cluster and the outer point charge layers that keep their formal ionic charges. This way the potential is reasonably accurate at some distance outside the cluster volume. This is in contrast with a recently published method that uses point charges only on spherical surfaces close to the outer cluster atoms (3).

Electronic Structure Calculations

In practice, heavy atoms—desired in gamma ray detectors—are modeled by effective core potentials (that include the relativistic effects experienced by the inner electrons) surrounded by valence electrons. This reduces the computational labor because the Schrödinger equation is solved only for the non-relativistic valence electrons. The first level of theory is the Hartree-Fock (HF) method, which minimizes the energy by varying the molecular orbitals of the individual electrons one at a time (assuming at each step that the others are frozen). The molecular orbitals are linear combinations of Gaussian basis functions chosen by the user. Note that while standard basis sets provide diffuse functions that are useful for describing covalent bonds, those for negative atoms are not sufficiently diffuse to describe excited electrons. For such calculations, it is necessary to add custom Gaussian basis functions to the negative ions with exponents from 0.01 to 0.05 Bohr^{-2}. In a subsequent step, second-order Møller-Plesset (MP2) corrections can be performed on the Hartree-Fock molecular orbitals to determine an energy correction that partly accounts for electron motion correlation.

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In the neutral ground-state crystal, the above calculation should produce a minimum energy when the atoms are in their normal lattice positions. However, when an electron is abruptly removed in an ionization event, neither the electronic nor the atomic configurations are at a minimum energy. To find the minimum energy configuration of the resulting hole state, the electronic wavefunction is assumed to find its minimum energy in a time that is short compared to the motion of the atoms (Born-Oppenheimer approximation). The atomic coordinates are then varied to minimize the energy; at each value of the atomic coordinates the Schrödinger equation is solved to determine the electronic structure and the energy of the system. The result is the relaxed electronic and atomic configuration after an electron has been removed (i.e., a lattice-relaxed hole).

To determine whether the hole can move in the host crystal, a cluster of atoms is used that is large enough to model a self-trapped hole located at two (or three, depending on symmetry) equivalent neighboring positions. If it can be shown that the hole can move among these locations, then the hole can diffuse throughout the host crystal. After determining the atomic configurations for a self-trapped hole at those locations, the configuration space is searched to find the minimum energy path from one hole to the next. The maximum energy along the path is the energy barrier for hole diffusion. If this energy barrier is less than kT (0.025 eV at room temperature), holes diffuse readily; if the energy barrier is very much greater than kT, the holes are trapped and not able to diffuse.

The Gaussian 94 program (4). at the Hartree-Fock (HF) and Møller-Plesset second-order perturbation theory (MP2) levels was used to determine energies and electron population distributions for cesium iodide. Excited state calculations used the CIS method (configuration interaction-singles) available in Gaussian 94. The runs were performed on a Silicon Graphics, Inc. computer with a four R10000 processors and on a Cray J-90 at the U.S. Department of Energy National Energy Research Supercomputer Center at the Lawrence Berkeley National Laboratory. Atomic charges and electron populations were determined from the Natural Population Analysis (NPA) phase of the Natural Bond Orbital (NBO) analysis (5). We used the Jaguar (Schrödinger, Inc.) program for the lead fluoride studies. The Jaguar runs were performed on Silicon Graphics, Inc. computers with a total of twelve R10000 processors.

FORMATION AND TRANSPORT OF HOLES IN CsI

To validate the computations and procedures, we use as a test material CsI, a scintillator of interest in both its pure and activated forms (6-10). From studies of CsI:Na and CsI:Tl it is known that energy transfer is a slow (≈ 10 ns) but efficient processes at room temperature. In addition, the existence of a V_k center—a bound I_2^- molecule aligned along the [100] axis—after x-ray irradiation has been observed in CsI doped with Na^+ and Tl^+ using optical and electron spin resonance techniques (11, 12). See Reference (13) for additional details of the computations summarized below.

In Fig. 1 the two central iodine atoms are allowed to move in the I_1–I_4 direction and their four nearest cesium neighbors are allowed to move radially in the coulomb field of the hole. The movable atoms are surrounded by a sufficient number of atoms to provide realistic interatomic forces.

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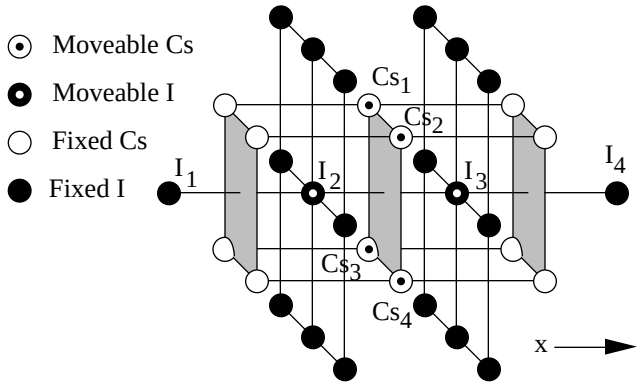

Figure 1. $Cs_{12}I_{20}$ **c**luster used to model hole formation in the CsI host crystal.

Hole Formation in $Cs_{12}I_{20}$

During hole relaxation the central iodine atoms I_2 and I_3 pulled together from an interatomic separation of 4.568 Å to 3.46 Å, and the four nearest neighbor Cs atoms moved radially outward (Δb = 0.19 Å). The electron population analysis found that the I_2 and I_3 charges were both –0.54. The relaxed hole is therefore a bound $[I_2I_3]^-$ molecule, the expected V_k center.

Hole Formation in $Cs_{16}I_{29}$

To provide a cluster sufficient to produce a V_k center on two symmetric sites in a realistic environment, we used a larger cluster $Cs_{16}I_{29}$ shown in Fig. 2. In this cluster the three I atoms are allowed to move in the x direction and the eight nearest Cs neighbors are allowed to move both along the x direction and radially in the coulomb field of the hole.

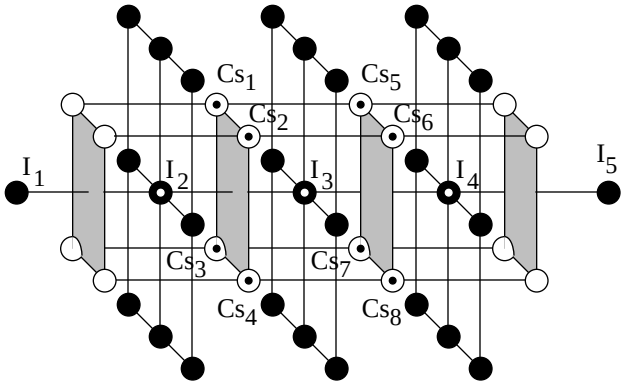

Figure 2. $Cs_{16}I_{29}$ cluster used to model hole formation and transport in the CsI host crystal. Atom symbols are the same as in Figure 1.

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At the normal lattice positions the electron population analysis yielded charges $q(I_2) = -0.92$, $q(I_3) = -0.16$, $q(I_4) = -0.94$, thus the hole was mainly on I_3 at the center of the cluster. A similar result has been reported for a hole in the NaCl lattice (13).

Optimizing the eleven movable atoms, the central iodine atoms I_3 and I_4 pulled together from an interatomic separation of 4.568 Å to 3.5 Å, and the four nearest neighbor Cs atoms moved radially outward ($\Delta g = 0.2$ Å). The electron population analysis found that the hole was now shared by I_3 and I_4, that is, $q(I_2) = -1.00$, $q(I_3) = -0.41$, $q(I_4) = -0.62$. (The inequality of $q(I_3)$ and $q(I_4)$ is a manifestation of the imperfect symmetry due to the different environments of the I_3 and I_4 atoms in the cluster used.) The relaxed hole is again a bound $[I_3I_4]^-$ molecule, thus the expected V_k center is found in both clusters $Cs_{12}I_{20}$ and $Cs_{16}I_{29}$.

Hole Transport in $Cs_{16}I_{29}$

Because a V_k center can be formed by either I_2-I_3 or I_3-I_4, depending on the x coordinate of I_3, we explored how a V_k center can be shifted between the two sites by varying the x coordinate of I_3 from 0.0 to 1.2 Å in discrete steps of 0.2 Å. At each value of the x coordinate of I_3, a ten-atom relaxation of the six position parameters was performed. Each of the seven six-parameter optimizations required approximately 300 hours of R10000 processor time.

Fig. 3 shows that by including the effects of electron correlation using Møller-Plesset second-order perturbation theory (MP2) , the binding of the V_k center increases. The importance of MP2 has been shown previously for hole formation in NaCl (14). The results in Fig. 3 show in addition that the transition state for hole transport in CsI along the 100 direction is an unstable one-center configuration that lies 0.15 eV above the relaxed V_k center configuration.

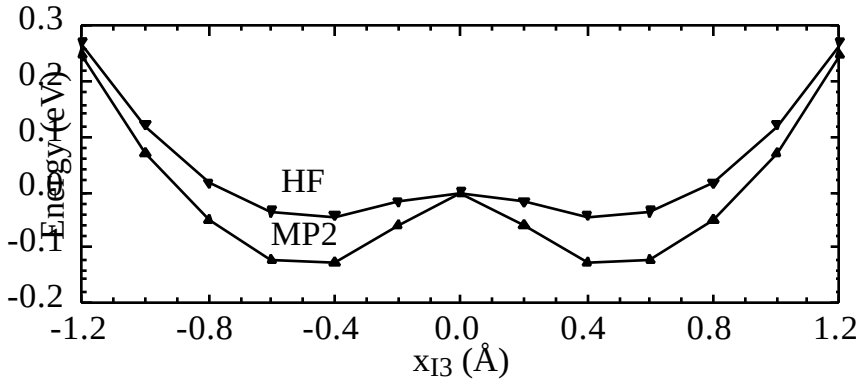

Figure 3. Energy at the HF and MP2 levels of theory as the x coordinate of I_3 is varied. The two stable configurations at $x_{I3} = -0.5$ Å and +0.5 Å are V_k centers at the I_2-I_3 and I_3-I_4 sites, respectively.

The rate of hole migration is also evident from the scintillation risetime. The risetime of the scintillation emission of CsI(Tl) has been carefully measured by Valentine, et al. (15) as a function of temperature. The measured risetime varied from 890 to 13 ns as the temperature was varied from -60 to 50 C°. These results yielded an activation energy of

0.23 eV. This was attributed to the migration of the V_k center to the Tl luminescence center and is in reasonable agreement with the computed barrier height of 0.15 eV in Fig. 3. It is anticipated that use of a larger cluster and more complete relaxation of the atoms surrounding the V_k state would increase the calculated value of the energy barrier, thus providing better agreement with experiment.

FORMATION OF THE EXCITED STATE OF CsI:Na

To model the formation of the excited state of Na in a CsI crystal, we used the $Cs_{12}I_{20}$ cluster with one of the Cs nearest the I_2-I_3 site replaced with Na as shown in Fig. 4.

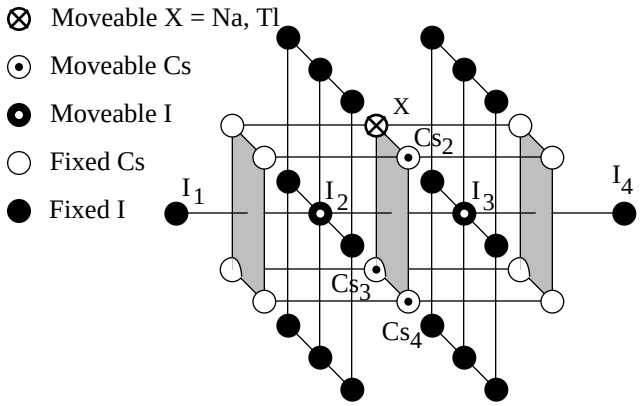

Figure 4: Cluster used to model hole and electron capture by Tl and Na atoms to form the excited state.

Ground State

The Na charge is +0.79 and the electronic orbital configuration is 3s(0.20), 3p(0.01). During relaxation the Na moves outward by 0.13 Å and the energy drops 0.02 eV.

Hole State

Before relaxation, the energy is 8.60 eV higher than the ground state. Relaxation reduces the energy by 1.2 eV to 7.43 eV above the ground state. In addition, relaxation reduces the I_2-I_3 distance, the Na atom moves radially outward by 0.54 Å, and the Cs atoms move outward by about 0.2 Å. The hole is located on atoms I_2 and I_3 which each have charge –0.50. The Na charge is +0.81 and the electronic orbital configuration is essentially unchanged from the ground state. Therefore the hole in CsI:Na appears identical to a V_k center in CsI. The Na atom acts as a spectator, moving outward in the coulomb field of the hole on I_2-I_3 . It moves 0.36 Å further than the other Cs atoms due to its smaller ionic radius.

Excited State

When the system is solved for the excited state (neutral triplet, using the CIS method), the energy is 4.81 eV above the ground state. Relaxation changes the atom coordinates and the energy by only a small amount. Relative to the ground state, the Na

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has gained 0.89 electrons and has an electronic configuration 3s(0.57), 3p(0.52) and the two nearest neighbor I atoms have each lost 0.51 electrons. Thus the excited state appears to be a V_k center near a Na atom that has captured an electron.

FORMATION OF THE EXCITED STATE OF CsI:Tl

The formation of the excited state of Tl in a CsI crystal, was modeled similarly using the $Cs_{12}I_{20}$ cluster with one of the Cs nearest the I_2-I_3 site replaced with Tl (Fig. 4).

Ground State

The Tl charge is +0.37 and the electronic orbital configuration is 6s(2.00), 6p(0.62), 7p(0.01). All eight nearest-neighbor I atoms have a charge of –0.93. All other Cs and I atoms have their nominal charges of +1.00 and –1.00, respectively. During relaxation the Tl moves outward by 0.05 Å and the energy drops 0.01 eV. These numbers are less than those for the case of Na in CsI:Na because Tl and Cs have more similar ionic radii.

Hole State

Before relaxation, the energy is 8.38 eV higher than that of the ground state. Relaxation reduces the energy by 0.04 eV and the atoms move very little ($\leq$ 0.10 Å). The hole is located on a single I atom (one of the eight nearest-neighbors to Tl) with charge –0.07. The Tl charge is +0.33 and the electronic configuration is essentially unchanged from the ground state. As shown in Fig. 4, the one-center hole is only ~0.05 eV above the V_k center at the HF level. It is possible that the one-center hole configuration is favored because of its proximity to the relatively negative Tl atom whose charge of +0.37 represents a –0.63 charge defect relative to the Cs atoms in the lattice.

Excited State

Using the CIS method, the excited state energy is 5.04 eV above the ground state. Relaxation changes the atom coordinates and the energy by only a small amount. Relative to the ground state, the Tl charge decreases by 0.17 to +0.20 and the excited electronic configuration is 6s(1.22), 6p(1.32), 7p(0.26) with the higher 6p and 7p orbitals gaining 0.95 electrons. All Cs and I atoms have essentially their ground state charges and electronic configurations and the excitation is localized on the Tl atom.

HOLE FORMATION AND TRANSPORT IN THE CRYSTAL PbF_2

Cubic lead fluoride has the calcite lattice structure. Preliminary calculations of a Pb_8F_{16} cluster embedded in 6,120 point charges showed that (1) in the ground state the occupied orbitals with the highest energy are on the Pb atoms, (2) when an electron is removed the hole is centered on a single Pb atom, and (3) moving a pair of neighboring F atoms from a Pb with a hole toward a neighboring Pb atom causes the hole to transfer to the second Pb atom. This is understandable, because when the two F atoms are moved toward a nearest Pb, it becomes energetically favorable for that Pb atom to have the extra

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positive charge. This situation differs significantly from the two-atom V_k center found in alkali halide crystals where the positive charge is shared between two halide ions.

The electron population analysis for this cluster also showed that the Pb and F atoms are not fully ionized, and had charge values of +1.8 and –0.9 respectively. For subsequent calculations, these values were used for the point charges.

A larger $Pb_{24}F_{48}$ cluster was then designed to allow the hole to occupy two equivalent nearest neighbor Pb sites (Fig. 5). The four-electron Los Alamos LACVP basis set ($6s^2 6p^2$) and associated 78-electron effective core potentials, a standard feature of Jaguar, was used for the Pb atoms and the 6-31G+ basis set was used for all F atoms. The most diffuse Gaussian basis functions had exponential coefficients of 0.06 $Bohr^{-2}$ and 0.10 $Bohr^{-2}$ for the Pb and F atoms, respectively. This cluster was embedded in 11,928 point charges that reproduced the Madelung potential to an accuracy of 2.2 mV rms over the atomic cluster volume.

With an electron removed and the central two Pb atoms and all their nearest eight F atoms (a total of 16 atoms) relaxed, the electron population analysis showed that the hole is centered on a single Pb atom, where 0.76 of an unpaired electron spin is on the Pb atom and the remaining unpaired spin is shared almost equally by the eight nearest neighbor F atoms. During the relaxation of the hole, the two movable Pb atoms increase their separation slightly from 4.20 Å to 4.29 Å while the eight F atoms nearest the hole are drawn in to the Pb hole center, their separation from the Pb decreasing from 2.57 Å to 2.33Å.

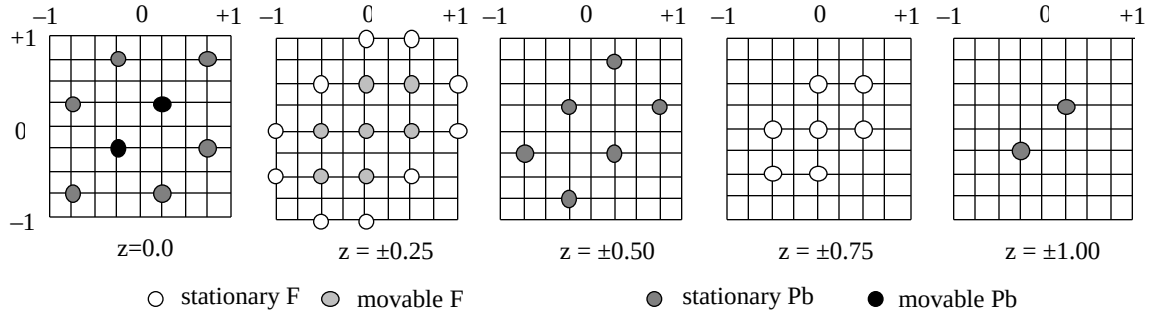

Figure 5. Schematic diagram of the Pb and F atomic layers of the $Pb_{24}F_{48}$ cluster used to model hole transport in PbF_2. Dimensions are in units of the unit call parameter $a_x = b_y = c_z = 5.94$ Å.

To investigate the transfer of a hole on one Pb to a nearby Pb, we introduce a configuration coordinate defined to be 0.0 for the relaxed hole on one Pb atom and 1.0 for the relaxed hole on the neighboring Pb atom. The calculated energies of the intermediate configurations (simple weighted averages of the two relaxed hole coordinates) is shown in Fig. 6. When the calculation was performed with a 6-31G basis set for the F atoms (most diffuse exponential coefficient 0.35 $Bohr^{-2}$), the results are close to those using the G-31G+ basis set (most diffuse exponential coefficient 0.10 $Bohr^{-2}$). In Figure 5, as the configuration coordinate increases from 0 to 0.49 the energy rises 1.11 eV above that of the relaxed hole and only a 0.01 of an electron spin is transferred to the nearest neighbor Pb atom. At a coordinate value of 0.5, the configuration and the wavefunction is symmetric so that the hole is shared equally between the two Pb atoms. However, this

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constraint results in a higher energy, 1.46 eV above that of the relaxed hole. For coordinate values above 0.5, the hole "hops" to the nearest neighbor Pb atom and the energy curve is symmetric about 0.5. The electron analysis of charge associated with each atom is consistent with the above spin analysis.

While photoluminescence has been observed from several activator atoms in crystals of PbF_2, scintillation has not (16). This may be attributed to the large barrier for hole transport to the activator.

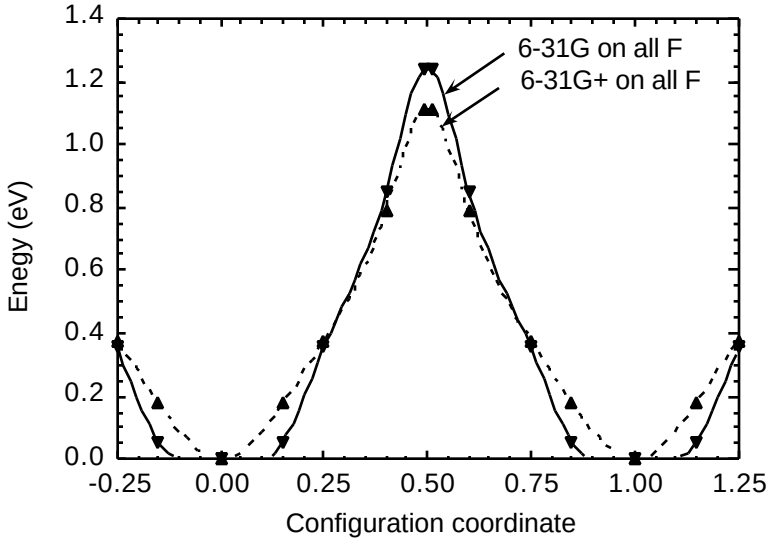

Figure 6. Calculated energy barrier for transfer of a hole on one Pb atom at 0.0 to a neighboring Pb atom at 1.0 in PbF_2.

HOLE FORMATION AND TRANSPORT IN THE CRYSTAL PbF_4

In contrast to Pb(II) which has two 6s outer electrons, Pb(IV) has a filled 5d outer shell and no 6s electrons. We have explored PbF_4 as a possible scintillator. (Other examples of Pb(IV) compounds are of the form A_2PbF_6, A_2PbO_3, $BPbF_6$ and $BPbO_3$, where A is a monovalent atom and B is a divalent atom.)

The PbF_4 crystal has a tetragonal lattice structure consisting of alternating planes, one containing Pb and F atoms (stoichiometrically PbF_2) and one containing only F atoms. The Pb atoms has six-fold nearest-neighbor F coordination, two in the F-only plane and four in the Pb-F plane. There are two different F sites, those in the F-only plane have two nearest neighbor Pb atoms (2.12 Å) and 12 nearest neighbor F; those in the Pb-F plane have one nearest neighbor Pb (1.97 Å) and 12 nearest neighbor F. The F atoms in the F-only plane are more weakly bound (10.8 eV) than those in the PbF_2 plane (13.8 eV). Preliminary calculations of a Pb_7F_{34} cluster embedded in 8,599 point charges showed that (1) in the ground state the occupied orbitals with the highest energy are associated with F atoms in the F-only planes and (2), when an electron is removed, the hole is centered on a single F atom in an F-only plane.

The electron population analysis for this cluster also showed that the Pb and F atoms are not fully ionized, and had charge values of +3.2 and –0.8 respectively. For subsequent calculations, these values were used for the point charges.

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A larger $Pb_{14}F_{56}$ cluster was then designed to allow the hole to occupy two equivalent nearest neighbor F sites in an F-only plane (Fig. 7). The four-electron Los Alamos basis set and associated effective core potentials was used for the Pb atoms and the 6-31G basis set was used for all F atoms except for the central two F atoms where the 6-31G+ basis set provided a better description of any covalent bond between those two F atoms. The most diffuse Gaussian basis functions had exponential coefficients of 0.06 $Bohr^{-2}$ and 0.10 $Bohr^{-2}$ for the Pb and F atoms, respectively. This cluster was embedded in 8,570 point charges that reproduced the Madelung potential to an accuracy of 0.5 mV rms over the atomic cluster volume.

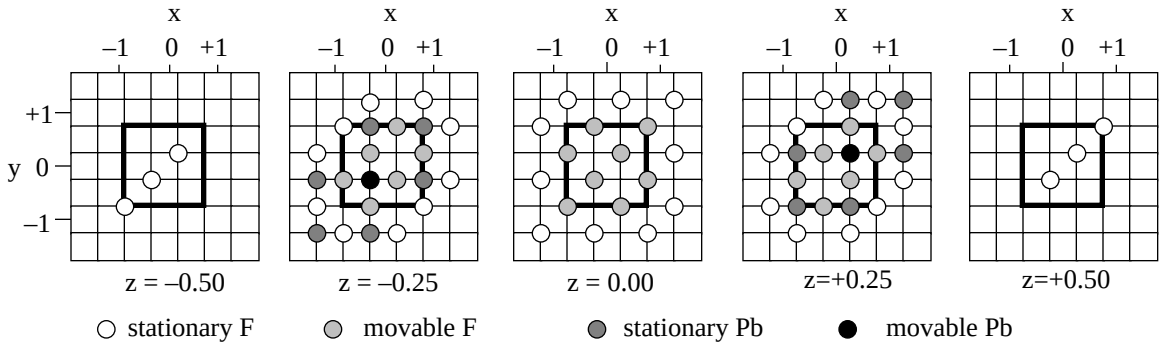

Figure 7. Schematic diagram of the Pb and F atomic layers of the $Pb_{14}F_{56}$ cluster used to model hole transport in PbF_4. Dimensions are in units of the unit cell parameter $a_x = b_y = 4.247$ Å, $c_z = 7.54$Å.

When the ground state cluster was constructed from the International Crystal Structure Database (Gmelin Institute, Germany) and allowed to relax, it was found that the atoms in the F-only plane reduced the bond length to their nearest neighbor Pb atoms from 1.97 Å to 1.85Å. To provide a stable structure that preserved the configuration of the F-only plane, it was necessary to decrease the crystal constant c_z from its database value of 8.03Å to 7.54 Å. It is possible that if the ten 5d Pb electrons were treated as quantum electrons rather than an effective core potential, the interatomic forces would be more accurate.

To investigate the transfer of a hole on one F to a nearby F, we again introduce a configuration coordinate defined to be 0.0 for the relaxed hole on one F atom and 1.0 for the relaxed hole on the neighboring F atom in the F-only plane. The calculated energies of the intermediate configurations (simple weighted averages of the two relaxed hole coordinates) is shown in Fig. 8. As the configuration coordinate increases from 0 to 0.49 the energy rises 1.11 eV above that of the relaxed hole and only a 0.01 of an electron spin is transferred to the nearest neighbor F atom. At a coordinate value of 0.5, the configuration and the wavefunction is symmetric so that the hole is shared equally between the two F atoms. However, this constraint results in a higher energy, 3.15 eV above that of the relaxed hole. For coordinate values above 0.5, the hole “hops” to the nearest neighbor Pb atom and the energy curve is symmetric about 0.5. The electron analysis of charge associated with each atom is consistent with the above spin analysis.

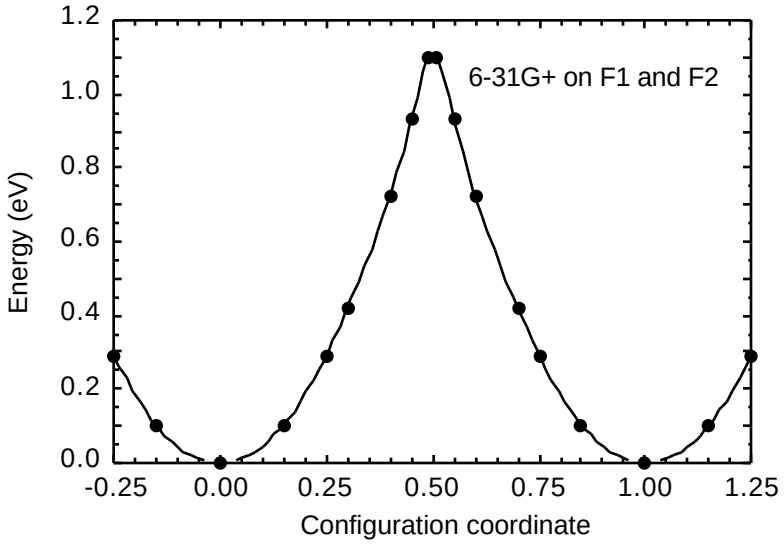

Figure 8. Calculated energy barrier for transfer of a hole on one F atom at 0.0 to a neighboring F atom at 1.0 in PbF_4.

Because of the large energy barrier for hole diffusion between F atoms in PbF_4, this material does not appear promising as a host compound for efficient activated scintillation.

DISCUSSION

This work was intended as a feasibility study of what could be done with currently available software and hardware. Clearly it would be desirable to extend this work using larger clusters of atoms in more complete states of relaxation, a larger number of basis functions, and the highest feasible level of theory. However these aspirations are severely limited by the computation time involved which can increase as the fourth power of the number of atoms. With respect to the methods used for the present calculations, considerable reduction in computation speed should be possible (i) using algorithms designed for more efficient convergence of the Hartree-Folk equations, (ii) using second derivatives for atom position relaxation, and (iii) replacing the ground-state boundary atoms with pseudopotentials (17) to preserve the interatomic forces while reducing the number of electrons in the calculation.

We conclude that it is now possible (although computationally intensive) to perform preliminary calculations of hole formation and transport, essential processes in scintillator crystals. Anticipated advances in software efficiency and computer speed should allow the systematic exploration of many other crystals to identify candidates for useful new scintillators.

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